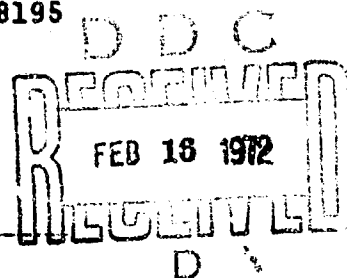


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KINETICS OF HYDROLYSIS OF OXYGEN DIFLUORIDE

By Sudhindra N. Misra and George H. Cady*



Abstract

Oxygen difluoride dissolves in water and reacts only very slowly with the solvent. In alkaline medium, however, the rate of hydrolysis is increased and follows the equation

$$\frac{d[\text{OF}_2]}{dt} = -k[\text{OF}_2][\text{OH}^-]^{\frac{1}{3}-0.0105}$$

At 20° the constant, k , has the value 4.1×10^{-3} , when time is in seconds and concentrations are in moles per liter. The energy of activation is about 8.5 kcal per mol.

INTRODUCTION

The basic hydrolysis of oxygen difluoride has previously been studied, but under such conditions that the rate controlling step was the rate of dissolving of the gas rather than the rate of hydrolysis when in solution.¹

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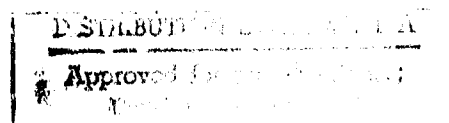
In the present study, the rate of disappearance of dissolved OF_2 was measured. Substantially no gaseous phase was present in the system. The total reaction was $\text{OF}_2 + 2\text{OH}^- = \text{O}_2 + 2\text{F}^- + \text{H}_2\text{O}$. (1)
Oxygen difluoride does not behave as the anhydride of an acid. It has only a low solubility in water² or even in cold 40% KOH.³

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2. O. Ruff and W. Menzel, Z. anorg. allgem. Chem., 198, 39 (1931).

3. R. A. Rhein and G. H. Cady, Inorg. Chem., 3, 1644 (1964).
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None of its reactions are known to produce the recently discovered molecule, HOF .⁴

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EXPERIMENTAL

Oxygen difluoride used in this study was a commercial product obtained from the Allied Chemical Company. When a sample of the gas was taken directly from the cylinder, its infrared spectrum showed no evidence for impurities. Fractional codistillation of a sample also gave indication of the presence of only one substance. In spite of this evidence for purity, the gas, before use in studies of its hydrolysis, was bubbled through 0.1M-NaOH to remove SiF_4 and other acidic gases which might have been present. The base would have caused the introduction of some oxygen into the OF_2 . This oxygen impurity should not have been harmful. Before making a run, a solution of OF_2 was prepared by shaking a sample of the gas with water held in a two liter flask.

Apparatus - The reactor was a vessel of polypropylene having a volume of 1245 ml. The vessel was 18 cm. in diameter and had a tight, but removable lid equipped with polypropylene fittings to hold the following items: (1) a fluoride ion sensitive electrode made by Orion Research, Inc., model 94-09, (2) a reference electrode for use with the fluoride electrode, (3) and (4) a glass electrode and reference electrode for use in measuring pH, (5) a thermometer. A Teflon covered magnetic stir-bar was placed in the vessel and was rotated during a run by a magnetic stirrer placed under the thermostat bath. Measurement of pH was made with a Leeds and Northrup 7400 A2 series meter. The emf of the cell involving the F^- sensitive electrode was measured with an Orion Research Specific Ion Meter, Model 401.

Procedure - A measured amount of solution of OF_2 was transferred to the reactor. Other reagents as desired were also added, and

the reactor, before use in a run, was caused to be completely filled with solution and closed with a loosely fitting plug. The vessel was placed in water held at constant temperature to within 0.1° . After the solution reached constant temperature, readings were made from time to time of the pH and F^{-} concentration. Many runs were made in buffered solutions containing sodium carbonate, sodium bicarbonate, and enough sodium nitrate to give a total ionic strength of 0.25 molar. In other runs the solution was made alkaline with sodium hydroxide, and the pH was allowed to change as the reaction occurred. A comparison of rate constants obtained by the two methods indicates that the presence of ions other than OH^{-} in the buffered solutions had little or no influence upon the rate of hydrolysis of OF_2 . Some of the runs were made with solutions more alkaline than pH 11. Since the fluoride sensitive electrode could not be used in this range, the concentration of dissolved OF_2 was measured by withdrawing a 25 ml sample of solution and adding it to a solution of potassium iodide. After adding dilute sulfuric acid in excess, the iodine was titrated with sodium thiosulfate solution. To keep the reactor filled so that OF_2 would not escape from solution, glass beads were added immediately after removal of the sample of solution. In runs involving use of the fluoride ion sensitive electrode the concentration of OF_2 was not observed directly. Along the course of a run, the concentration of F^{-} ion was measured at intervals. At the termination of a run the solution was allowed to stand until substantially all of the OF_2 had reacted. The molar concentration of dissolved OF_2 at any stage of the run could then be calculated by considering it to be half as great as the increase in molarity of F^{-} from

that time until all of the gas had reacted.

During the course of the work the pH meter was tested frequently with buffer solutions. The fluoride sensitive electrode was also checked frequently using solutions containing F^- of known molarity, pH and ionic strength. Because of this method of calibration, the electrode as used gave F^- concentrations in moles per liter. From readings of the pH meter, the corresponding activities of OH^- in moles per liter were calculated. The fluoride-ion sensitive electrode behaved in the manner reported by the manufacturer toward F^- concentration and influence of ionic strength. Because of interference by OH^- ion, the electrode was not used at pH in excess of 11.

RESULTS

Observed data are represented within the limits of experimental accuracy in Figs. 1 to 4. Fig. 1 represents four runs at 20.0° using solutions buffered at different values of pH. These runs together with others not shown indicate that at constant pH and temperature the rate is directly proportional to the concentration of OF_2 . Fig. 2 represents a run at 20.0° in which OF_2 reacted with a solution of sodium hydroxide while the pH was allowed to change as hydrolysis occurred. From the shape of the curve it is apparent that a decrease in the concentration of OH^- ion causes a decrease in the rate of reaction. If one draws a tangent to the curve at a selected value of pH, the slope is the same (within experimental accuracy) as a straight line in Fig. 1 for the same pH. Numerous runs of this type were made, some at pH values greater than 11.

At constant pH, the rate follows the equation $\frac{d[\text{OF}_2]}{dt} = -k'[\text{OF}_2]$

To evaluate k' as a function of $[\text{OH}^-]$, graphs were drawn in which k' was plotted vs. various powers of the molarity of OH^- . Fig. 3 shows that at 20° in the pH range 9.6 to 11.5 the value of k' is directly proportional to $\{[\text{OH}^-]^{\frac{1}{3}} - 0.0105\}$. The rate equation may, therefore, be written as

$$\frac{d[\text{OF}_2]}{dt} = -k[\text{OF}_2] \{[\text{OH}^-]^{\frac{1}{3}} - 0.0105\}$$

In the evaluation of k' and k , time was measured in seconds. The straight line in Fig. 3 corresponds to k having a numerical value at 20°C of 4.1×10^{-3} when time is in seconds and concentrations are in moles per liter.

The three highest points in Fig. 3 were obtained using iodometric titration of dissolved OF_2 as it was reacting with a solution of NaOH . The other points were obtained using the fluoride-ion sensitive electrode as the dissolved OF_2 reacted either with a solution of NaOH or with a buffered solution containing Na_2CO_3 , NaHCO_3 and NaNO_3 . Most of these points were obtained for buffered solutions.

Runs were made using buffered solutions at $\text{pH} = 10.0$ at 25.0° and 30.0° . From these runs, values of k were calculated. Fig. 4 shows the relationship between $\ln k$ and the reciprocal of absolute temperature. The slope of the line in this figure corresponds to an energy of activation of 8.5 kcal per mole.

Acknowledgment: This research was performed in part under contract with the Office of Naval Research.

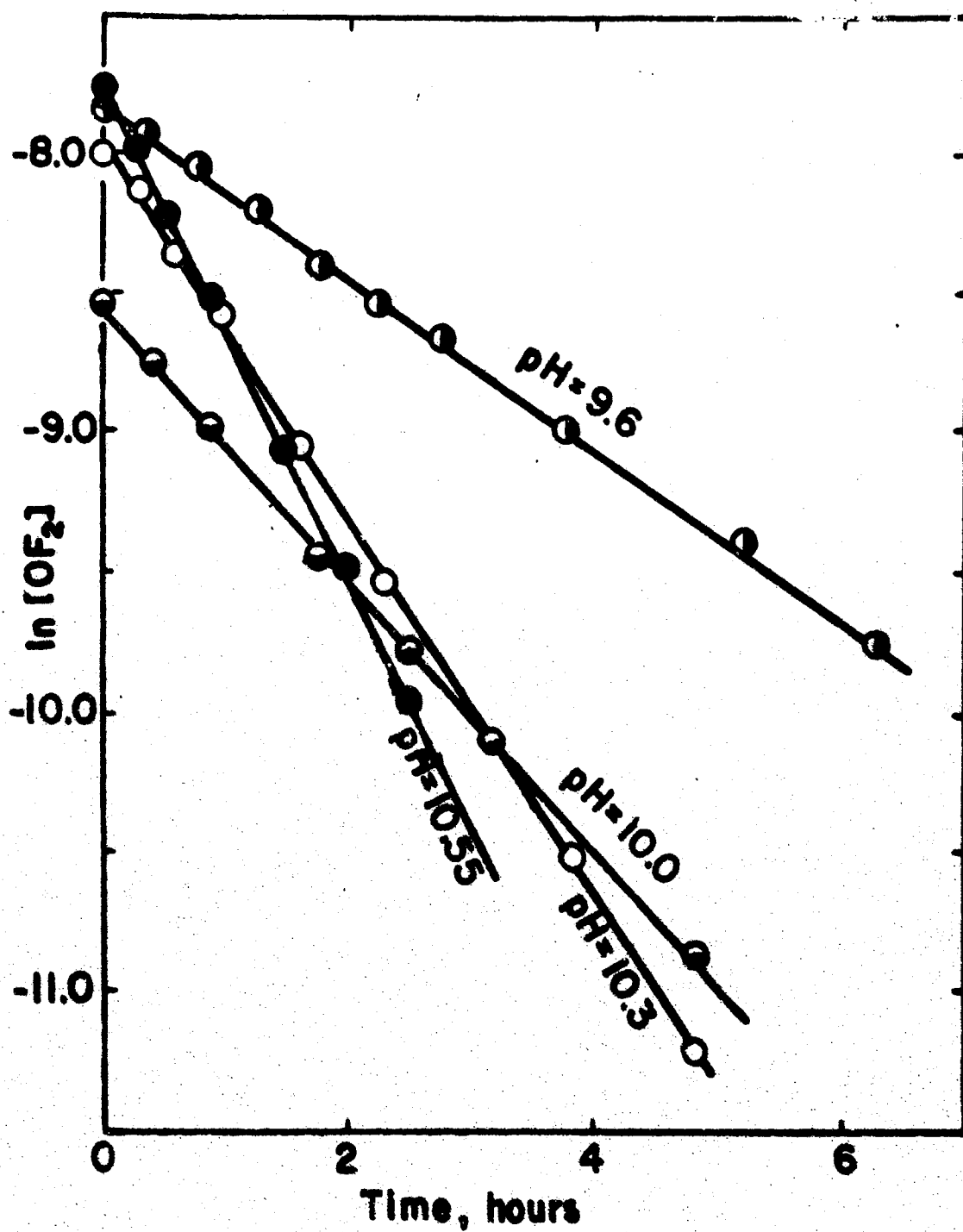


Fig. 1 - Rate of hydrolysis at 20.0° in buffered solutions.

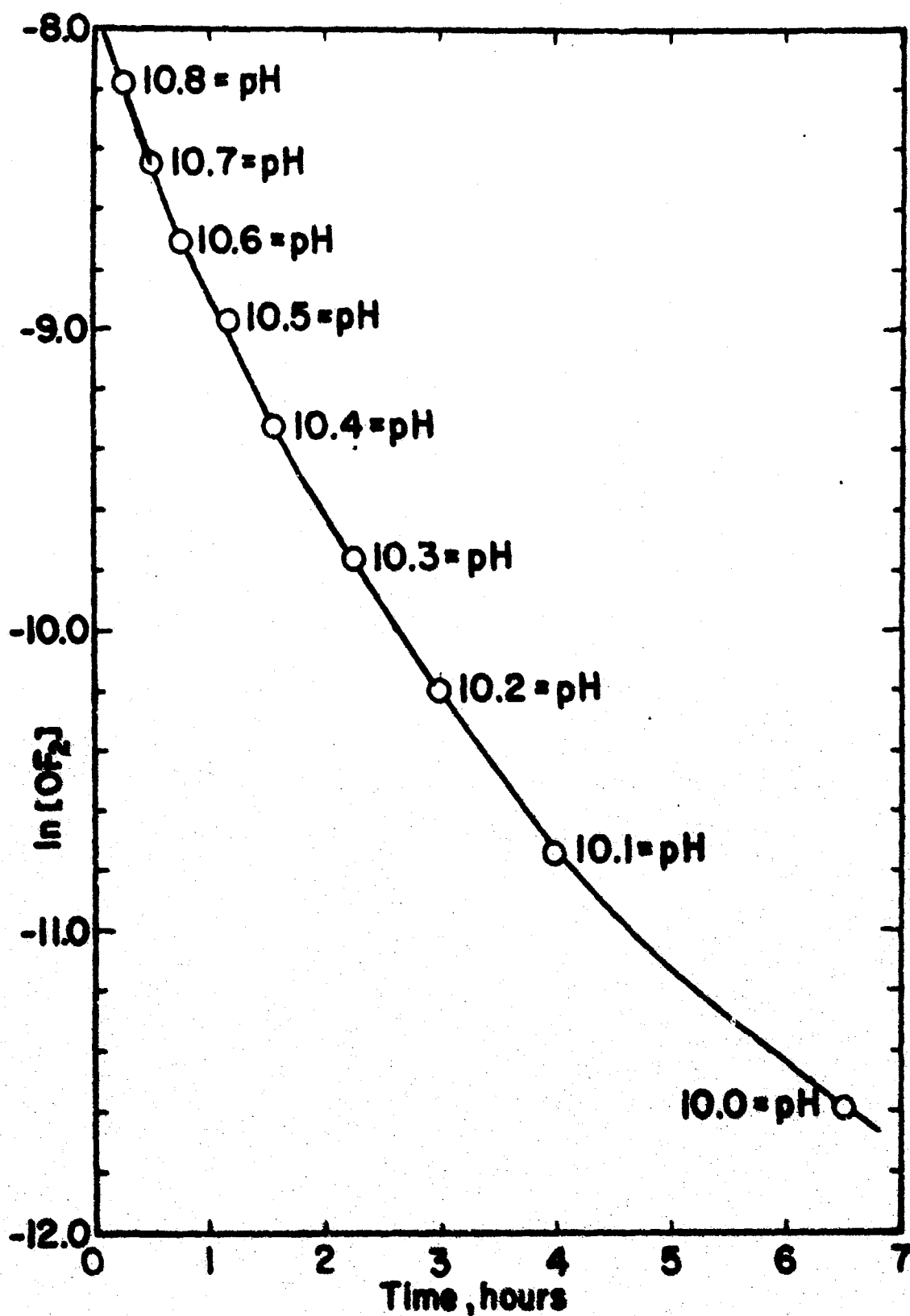


Fig. 2 - Rate of hydrolysis of OF_2 in a solution of sodium hydroxide at 20.0° . Concentrations of OF_2 and of OH^- decrease as time passes

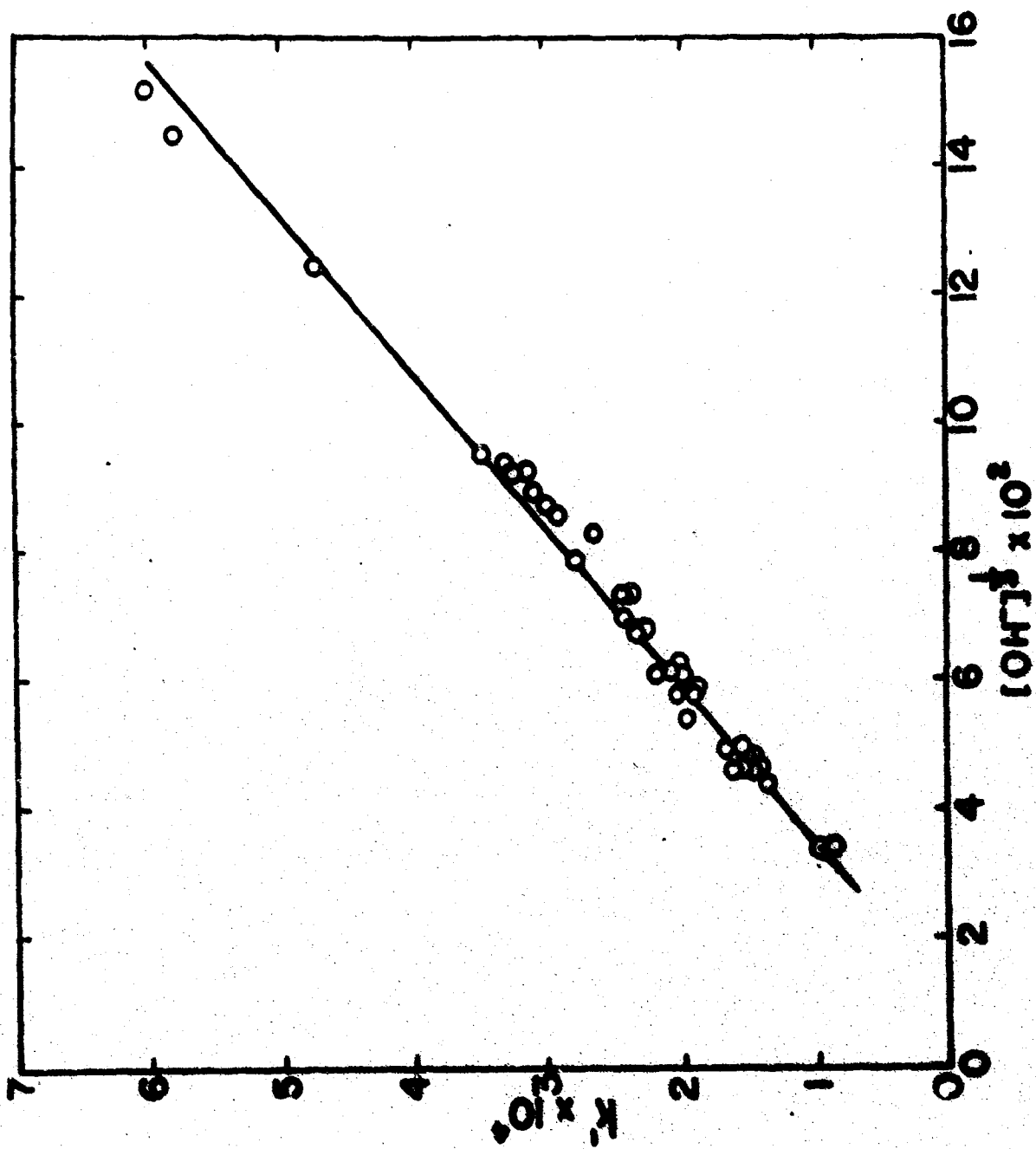


Fig. 3 - Relationship between k' and $[\text{OH}^-]^{1/2}$ at 20.0°.

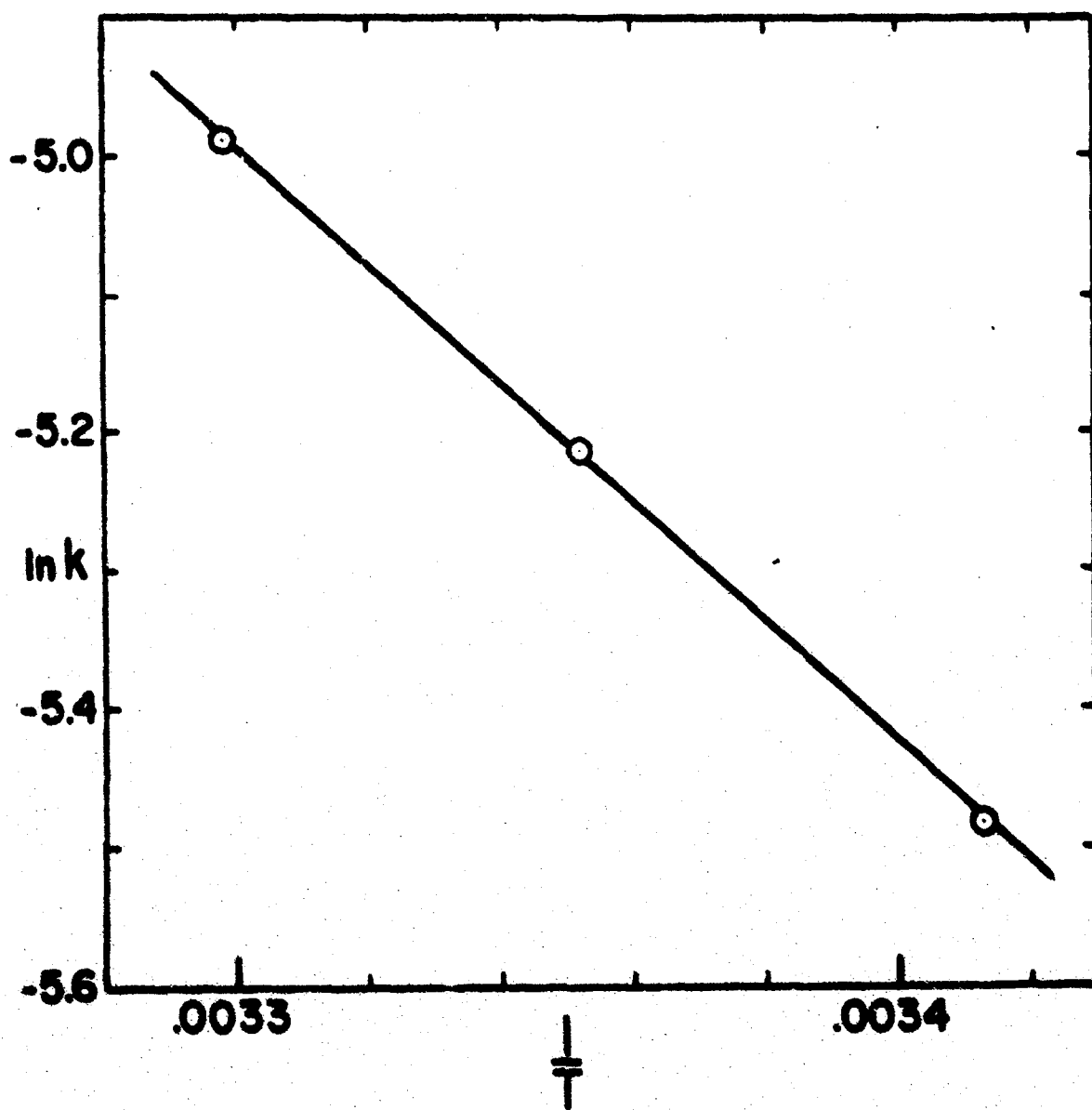


Fig. 4 - Relationship between $\ln k$ and $1/T$ when k is the rate constant in the equation $\frac{d[OF_2]}{dt} = -k[OF_2]([OH^-])^{0.0105}$

None

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
University of Washington Seattle, Washington		None	
3. REPORT TITLE		2b. GROUP	
Kinetics of Hydrolysis of Oxygen Difluoride			
4. DESCRIPTIVE NOTES (Type of report and, inclusive dates)			
Technical Report (1972)			
5. AUTHOR(S) (First name, middle initial, last name)			
Sudhindra Misra and George H. Cady			
6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS	
Jan. 1972	9	4	
8a. CONTRACT OR GRANT NO.	8b. ORIGINATOR'S REPORT NUMBER(S)		
N 00014-67-A-0103-0002	70		
9. PROJECT NO.	10. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
NR 093-018	None		
11. DISTRIBUTION STATEMENT			
Distribution of this document is unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		Office of Naval Research	
13. ABSTRACT			
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DD FORM 1473

(PAGE 1)

S/N 0101-007-0011

None

Security Classification

A-01-001

None

Security Classification

13.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Oxygen difluoride Oxygen difluoride, hydrolysis						

DD FORM 1473 (BACK)

1 NOV 65

None

Security Classification

A-314